Heat of Dilution of Cesium Chloride

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The heat of dilution of CsCl at 25° C. was determined at concentrations of 1.5, 2.0, 2.5, and 3.0 m. The excess entropy, $\overline{S}^E$, was calculated from the experimental heat of dilution and compared to the entropy expected for a "normal" electrolyte. The experimental and normal values differ greatly, confirming the conclusion from other evidence that CsCl is ion-paired to an appreciable extent.

$\mathbf{W}$HEN these measurements were started, the heat of dilution of CsCl had not been reported above 1.1 molal. Recently, Stakhanova et al. (8) reported values of ϕ_L from 2.0 to 5.0m, which differed appreciably from the present results.

EXPERIMENTAL

The calorimeter, experimental procedure, and CsCl solution have been described in detail elsewhere (4, 7, 10). Briefly, the calorimeter is a 60-ml. Dewar flask stirred by a magnetic stirrer. The temperature is sensed by a thermistor and electrical calibration is used. Tests (7, 10) show that for high heats the calorimeter is accurate to about ±1%, and for low heats the accuracy is about ±0.01 cal. The initial temperature was adjusted to 25.00 ± 0.02° C. and the pipette was opened. Electrical calibration followed completion of the measurement of the heat of dilution.

TREATMENT OF DATA

The values of $\Delta\phi_L$ were calculated from the data using the equation

$$\Delta\phi_L = -q/n \qquad (1)$$

where q is the heat given out and n is the moles of CsCl. The equation for the thermistor is

$$\Delta T' = \frac{R_i - R_f}{R_i + R_f} (T_i + T_f)^2 \qquad (2)$$

where R_i and R_f are the initial and final thermistor resistances, and T_i and T_f are the initial and final temperatures. The average heat capacity is

$$Cp = \frac{q}{\Delta T'} \qquad (3)$$

and therefore

$$\Delta\phi_L = (Cp/n)\Delta T' \qquad (4)$$

The relative apparent molal heat content at the initial concentration, $\phi_L(m_i)$, was calculated from the value of $\Delta\phi_L$ obtained above and the relative apparent molal heat content at the final concentration, $\phi_L(m_f)$, by the equation

Table I. Heat of Dilution of CsCl at 25° C.

m_i	m_f	q, Cal.	$\phi_L{}^a(m_f)$, Cal./Mole	$\Delta\phi_L$, Cal./Mole	$\phi_L(m_i)$, Cal./Mole	$\phi_L{}^b(m_i)$, Cal./Mole
1.5	0.2123	3.206	35.6	271.7	−236.1	
1.5	0.2040	3.083	37.2	273.1	−235.9	
1.5	0.2168	3.296	34.7	271.5	−236.8	
				Average	−236.3	
2.0	0.2837	5.640	20.6	357.4	−336.8	
2.0	0.2684	5.326	23.8	359.4	−335.6	
2.0	0.2881	5.748	19.7	357.0	−337.3	
				Average	−336.6	−347.0
2.5	0.2330	4.234	31.3	443.9	−412.6	
2.5	0.2423	4.406	29.3	440.1	−410.8	
2.5	0.2398	4.357	29.9	441.5	−411.6	
				Average	−411.7	−423.6
3.0	0.2850	5.969	20.3	510.2	−489.9	
3.0	0.2725	5.583	23.0	511.7	−488.7	
3.0	0.2787	5.871	21.7	512.7	−491.0	
				Average	−489.9	−494.6

[a] From Parker's low-concentration data, NSRDS-NBS 2, April 1965.
[b] Calculated from Stakhanova et al (8), using Parker's value at $m = 1.0$.

$$\Delta\phi_L = \phi_L(m_f) - \phi_L(m_i) \qquad (5)$$

The value for $\phi_L(m_f)$ was obtained from Parker's low-concentration data (5).

RESULTS AND DISCUSSION

Table I shows the heat of dilution of CsCl at 25° C. The last column in this table shows the values of ϕ_L calculated from the data of Stakhanova et al. (8), together with Parker's (5) value at $1m$. The present results are 5 to 12 cal. per mole more positive. This could be due to an error of this magnitude in Parker's value at $1m$.

Wood (9) showed that the partial molal entropies of normal strong electrolytes followed a single family of curves and could be correlated by a single parameter for each ion. The low-concentration data then available indicated that CsCl did not follow this correlation and was an "abnormal" electrolyte. The present results confirm this conclusion. The values of $T\bar{S}^E$ were obtained from the equation (9)

$$T\bar{S}^E = \bar{L}_2 - \bar{G}^E = \phi_L + m\ (d\phi_L/dm) - \nu RT \ln \gamma^{\pm} \qquad (6)$$

using the values of $\gamma^{\pm}$ from Robinson and Stokes (6) together with the ϕ_L from these measurements. The values of $d\phi_L/dm$ are from the slope of a large-scale graph of ϕ_L vs. m, using the present results and those of Parker.

The experimental values for $T\bar{S}^E$ are -385, -431,

and -659 cal. per mole for $m = 1.5$, 2.0, and 3.0, respectively, as compared to the values predicted for a normal electrolyte (9) of 190, 45, and -179 cal. per mole for $m = 1.5$, 2.0, and 3.0, respectively. The most likely reason for abnormal behavior is ion-pairing, and there is other evidence to support the hypothesis that CsCl is ion-paired (1, 2, 3).

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Heats of Mixing of Some Aqueous Alkali Metal Chloride Solutions

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The heats of mixing CsCl with LiCl, CsCl with KCl, and KCl with LiCl were determined at various ionic strengths. The heat of mixing CsCl with KCl was very small and the coefficient RTh_0 changed rapidly with concentration, indicating that the like-charged pair interactions are smaller in this mixing and about as important as triplet interactions. For the CsCl with LiCl and KCl with LiCl mixings, the coefficient RTh_0 changed fairly slowly with concentration, indicating that like-charged pair interactions contribute more to RTh_0 than triplet interactions.

IN CONNECTION with a study of the heat of mixing alkaline earth chlorides with alkali metal chlorides, the heats of mixing CsCl with LiCl, CsCl with KCl, and KCl with LiCl were needed at ionic strengths of 1, 2, and 3. Wu et al. reported results at unit ionic strength (10). Stakhanova et al. (3) measured the heats of mixing LiCl with KCl and LiCl with CsCl, but their results were not accurate enough for our purposes.

EXPERIMENTAL

The lithium chloride and potassium chloride stock solutions were prepared from reagent grade salts. All impurities reported for these salts were less than 0.01%. The stock solutions were analyzed for chloride in a gravimetric silver chloride precipitation. The pH of both solutions was between 5 and 6.5.

Table I. Results of the Heat of Mixing Experiments at 25° C.

Mixture	I	N^a	$RTh_0{}^b$	$RTh_1{}^b$
CsCl–LiCl	0.5	6	-172 ± 11	-13 ± 11
	1	4	-192 ± 6	-7 ± 11
	2	5	-215 ± 4	-17 ± 7
	3	6	-229 ± 3	-22 ± 5
CsCl–KCl	1	7	8.0 ± 0.9	0.0 ± 1
	2	6	2.8 ± 0.2	-0.3 ± 0.4
	3	6	-1.7 ± 0.4	-0.7 ± 0.7
LiCl–KCl	2	8	-80.4 ± 0.5	-3.8 ± 0.7
	3	15	-93 ± 1	-5 ± 2

[a] N is the number of experiments.
[b] Units are cal. per kg. of solvent per ional[2] (Equation 1).